HHS Public Access

Author manuscript

J Esthet Restor Dent. Author manuscript; available in PMC 2020 March 01.

Published in final edited form as:

J Esthet Restor Dent. 2019 March ; 31(2): 153–159. doi:10.1111/jerd.12437.

Optical properties and colorimetric evaluation of resin cements formulated with thio-urethane oligomers

Atais Bacchi, DDS, PhD[a,b], **Ricardo Armini Caldas, DDS, PhD**[c], **Paulo Francisco Cesar, DDS, PhD**[a], and **Carmem Pfeifer, DDS, PhD**[d,*]

[a]Department of Biomaterials and Oral Biology, University of São Paulo-USP, São Paulo, Brazil

[b]Department of Prosthodontics and Dental Materials, Meridional Faculty – IMED, Passo Fundo, Brazil

[c]Department of Prosthodontics and Periodontics, Piracicaba Dental School, Campinas State University, Piracicaba, Brazil

[d]Department of Biomaterials and Biomechanics, Oregon health & Science University, Portland, USA.

Abstract

Objective: The aim of this study was to evaluate the color parameters and optical properties of resin cements (RCs) formulated with thio-urethanes (TUs).

Materials and Methods: Six TUs were synthesized by combining thiols (pentaerythritol tetra-3-mercaptopropionate (PETMP) or trimethylol-tris-3-mercaptopropionate (TMP)) with di-functional isocyanates (1,6-Hexanediol-diissocyante (HDDI) (aliphatic-AL) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic-AR) or Dicyclohexylmethane 4,4'-Diisocyanate (HMDI) (cyclic-CC)). Thio-urethanes (20 wt%) were added to a BisGMA/UDMA/TEGDMA matrix. Filler was introduced at 60 wt%. Fluorescence was evaluated through an UV-light emitting equipment. Coordinates L*, a* and b* were obtained in the black and white reflectance to evaluate the contrast ratio (CR) and translucency (TP_{00}). The coordinates obtained from transmittance were used to evaluate lightness (L*), chroma (C*), color difference (ΔE_{00}) after 6 month, and whiteness index for Dentistry (WI_D).

Results: RCs formulated with TUs presented significantly higher CR, and fluorescence (with T_AR). Significantly lower C*, L*, and TP_{00} (except for P_AR and T_AL) were also observed in RCs containing TUs. ΔE_{00} were not significant among the materials. WI_D was not influenced.

Conclusion: Resin cements composed by thio-urethane oligomers present higher contrast ratio and lower translucency. The material also present higher fluorescence depending on the oligomer used.

*****Corresponding author:** Carmem S. Pfeifer, DDS, PhD, Assistant Professor, Oregon Health and Science University, Biomaterials and Biomechanics, 611 SW Campus Dr, rm 501, Portland, OR, USA 97239, Tel: 503-494-3288, Fax: 503-494-8260, pfeiferc@ohsu.edu.

Disclosure statement

The authors declare no conflict of interest.

Clinical Significance: The use of thio-urethanes to formulate resin cements can ensure a luting material with improved potential to mask colored substrates due to the higher contrast ratio and lower translucency obtained. A final higher fluorescence of restoration is also expected with the use of specific oligomer.

Keywords

resin cements; optical properties; colorimetric evaluation; thio-urethane oligomers

Introduction

Resin cements (RCs) have been emphasized as bonding agents in the last years because of several advantages over traditional zinc-phosphate or glass-ionomers cements, such as their ability to bond both to the restorative materials and to the tooth tissues, their lower water sorption and solubility, lower wear, and higher mechanical properties. RCs have rapidly become popular after their introduction and currently represent the main luting option for most prosthetic applications.[1]

Luting agents should be able to maintain marginal integrity of the restoration and to resist the tensile and shear stresses resulting from functional activity. Recently, experimental RCs formulated with thio-urethane oligomers have been explored.[2–4] These oligomers have pendant thiols that undergo a chain-transfer reaction with the surrounding methacrylate organic matrix.[5] RC compositions containing oligomers showed improved chemical-mechanical properties of interest for clinical applications. The main benefits of the presence of thio-urethanes in RC formulations were the increase in degree of conversion and the toughening of the polymer network, given by the addition of a flexible oligomer capable of multiple crosslinks. Properties such as water sorption and solubility were reduced, and mechanical properties were increased, especially Young's modulus and fracture toughness.[2–4]

Another important feature that needs to be present in RCs is the capacity to maintain the appropriate color appearance of the final restoration. The addition of such oligomers to a secondary matrix might provide significant optical benefits to the RCs, as their presence increases the refractive index of the polymer,[6,7] making it more compatible with the refractive index of the inorganic filler particles, therefore increasing overall light transmittance of the composite. However, other color parameters of these novel thio-urethane based cements, and markedly their effects on color and optical properties, have not been investigated.

The aim of this study was to evaluate the optical properties and color parameters of RCs after the addition of thio-urethane oligomers into the composition. Six oligomers were formulated by the combination of isocyanates and thiols. Thio-urethanes were combined with an organic matrix composed by BisGMA/UDMA/TEGDMA, resulting in six experimental RCs. One RC without oligomer served as control. The optical properties evaluated were the translucency parameter, contrast ratio, and fluorescence, and the colorimetric evaluation included whiteness index for dentistry, lightness, chroma, and color differences after water storage. The null hypotheses were that the use of thio-urethane oligomers for resin cements does not affect either (I) the color or (II) the optical properties of the RCs at initial and after 6 months periods.

Materials and Methods

Materials composition

Resin cements were formulated with Bis-phenol A diglycidyl dimethacrylate (Bis-GMA; Esstech, Essington, PA, USA), urethane dimethacrylate (UDMA; Esstech, Essington, USA) and tri-ethylene glycol dimethacrylate (TEGDMA; Esstech, Essington, USA) in a 50:30:20 mass ratio. Photoinitiators were added to the monomers as follows: 0.6 wt% of a tertiary amine (EDMAB - ethyl 4-dimethylaminobenzoate; Avocado, Heysham, England), 0.2 wt% of dl-camphoroquinone (Polysciences Inc., Warrington, PA, USA), and 0.5 wt% inhibitor (BHT - 2,6-di-tert-butyl-4-methylphenol; SigmaAldrich, St. Louis, MO, USA).

Six thio-urethane oligomers were synthesized as described previously.[8–10] Information about the oligomers used in the study is presented in Table 1. Thio-urethane oligomers were added to the methacrylate organic phase in proportion of 20 wt%, as defined in a previous investigation.[3]

Filler was introduced at 60 wt% (Barium glass 0.7 μm, density 3.0 g/ml, refractive index 1.553 - V117 4107, Esstech, Essington, USA), with the aid of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA) for 5 min at 2400 rpm. All procedures were carried out under yellow lights.

Specimen preparation

Specimens discs of 10 mm in diameter and 1.0 mm in thickness (n=5) were produced. Resin cement was applied and laminated between two glass slides and irradiated for 60 s at 700 mW/cm^2 (Bluephase, Ivoclar vivadent, Lichtenstein), with the light source in direct contact with the glass slide mold. Specimens were carried out by the same operator in order to avoid variability in fabrication and handling. Samples were stored for 72 h in dark containers before the first evaluation, and for an additional 6 months in distilled water for all parameters, as detailed below. All procedures were carried out at room temperature.

Fluorescence

The degree of fluorescence was measured using a spectrometer (Fluorescence System, Biopdi, São Paulo, Brazil) with a wavelength range of 405±15 nm. After calibration, the specimens were placed on the base of the equipment and an UV-light ray was emitted directly onto the specimen surface. Pictures of samples were obtained while using a LED and a green filter, allowing only emission of UV-light. Fluorescence is measured by means of quantifying the green pixels in the image, as a green filter determines how much ultra-violet light was reflected as green light, which corresponds to the fluorescence phenomenon. Images were analyzed with the software (Fluorescence System, Biopdi) and the fluorescence degree of experimental resin cements was determined and calculated in terms of percentage in comparison to a fluorescence standard (reference material) (Variolink Veneer, Ivoclar vivadent, transparent, lot T37843) that was considered as 100% fluorescence.[11]

Optical properties and colorimetric evaluation

Spectral data of resin cements was measured in transmittance and diffuse reflectance mode with a spectrophotometer (DM-3700d, Konica Minolta Inc., Chiyoda-ku, Tokyo, Japan) in the wavelength range of λ=360–740 nm/intervals of 10 nm. CIEL*a*b* color coordinates were calculated according to the CIE D65 Standard Illuminant and CIE 2° Standard Observer.

For reflectance, the color parameters of each experimental group was measured in three coordinate dimensions of L* [from 0 [black] to 100 [white]), a* green-red (−a*=green; +a*=red), and b* blue-yellow (−b*=blue; +b*=yellow). Measurements of reflectance were performed using white background (standard calibration tile with CIE L*=91.57, a*=−1.04, b*=7.02) and black background (standard calibration tile with CIE L*=26.62, a*=0.09, b*= −0.31).

Data obtained in the reflectance analysis were used to evaluate the contrast ratio and translucency parameter (TP_{00}). The results from transmittance were used to evaluate lightness (L*), coordinates a* and b*, chroma (C*), color difference after 6 month (ΔE_{00}), and whiteness index for Dentistry.

Contrast ratio

The contrast ratio represents the ratio of the luminous reflectance of a material over a black background to the luminous reflectance of the same material over a white background. When the two luminous reflectance values are the same, the material is completely masking the substrate and it presents the highest contrast ratio possible that is 1. Therefore, the highest the contrast ratio the highest the opacity of a material because it means that light is reflected irrespective of the background used.[12] The reflectance spectra of each resin cement was obtained in the wavelengths from 360 to 740 nm. The sum of the reflectance values in black (Y_b) or white backgrounds (Y_w) along the wavelengths of 360–740 nm is calculated for obtaining the contrast ratio as follows (1)[13]:

$$CR = Y_b / Y_w \quad (1)$$

Whiteness index for dentistry

Explaining in spectral terms, the whiter the material the higher and more constant is the reflectance across the visible wavelength range (near to 100% or reflectance value of 1).[14,15] These characteristics have been considered important because of recent highly esthetic demanding materials. The whiteness index for Dentistry was calculated using the L*, a* and b* parameters of transmittance analysis, as the following equation (2)[15]:

$$WI_D = 0.511L^* - 2.324a^* - 1.100b^* \quad (2)$$

Higher WI_D values indicate whiter samples, while lower WI_D values (including negative values) indicate darker samples.

Translucency parameter (TP_{00})

The CIEDE2000 was used to evaluate the translucency parameter of materials. In this parameter, the lower the TP_{00} value the more opaque the material is, providing higher masking ability.[12] TP_{00} is calculated from coordinates L*, a*, and b* measured in reflectance mode over black and white backgrounds for the same sample, as follows (3)[16]:

$$TP_{00} = \left[\left(\frac{L'_B - L'_W}{K_L S_L} \right)^2 + \left(\frac{C'_B - C'_W}{K_C S_C} \right)^2 + \left(\frac{H'_B - H'_W}{K_H S_H} \right)^2 + R_T \left(\frac{C'_B - C'_W}{K_C S_C} \right) \left(\frac{H'_B - H'_W}{K_H S_H} \right) \right]^{\frac{1}{2}} \quad (3)$$

TP_{00} is the translucency parameter, the subscripts “B” and “W” refer to lightness (L′), chroma (C′), and hue (H′) of the specimens over the black and the white backgrounds, respectively. RT is a function (the so-called rotation function) that accounts for the interaction between chroma and hue differences in the blue region. S_L, S_C, and S_H are the weighting functions and K_L, K_C, K_H are the correction terms to be adjusted according the experimental conditions.[17] The parametric factors K_L, K_C, K_H were set to 1.[18]

The same equation was used to measure the color difference (ΔE_{00}) of each resin cement before and after 6 months of water storage. That means the amount of color alteration suffered by one material over the six months. The color parameters L*, a*, and b* were obtained through transmittance mode. As defined previously, the color difference can be perceived over values of $\Delta E_{00} = 0.81$ (perceptibility threshold), and the color difference is considered acceptable up to $\Delta E_{00} = 1.77$ (acceptability threshold).[19]

Statistical analysis

Color difference registered in the 6 month represented by ΔE_{00} were evaluated with one-way ANOVA. The other analyses comparing data initially and after 6 months were evaluated by two-way ANOVA (evaluation period vs type of resin cement). Multiple comparisons were done using Tukey’s test. All tests were carried out at a global level of significance of 95%.

Results

Significance and interactions

The evaluation period ($p<0.001$) and the type of resin cement ($p<0.001$) significantly influenced the fluorescence, translucency parameter, contrast ratio, W_{ID}, lightness, and chroma. Interaction between the two factors were observed for fluorescence ($p=0.002$), translucency parameter ($p=0.001$), contrast ratio ($p<0.001$), W_{ID} ($p<0.031$), and chroma ($p<0.029$). Interaction was not significant for lightness ($p<0.268$).

Fluorescence

In the initial evaluation, the highest fluorescence level value was observed in the resin cement formulated with the T_AR version of oligomer (12.3% higher than control), which showed similar fluorescence to T_AL. The fluorescence of groups with oligomers P_AL and P_AR were significantly lower than that of the control. After 6 months, the highest value of fluorescence was still that of T_AR (21.7% higher than control), which was similar to the values obtained by T_AL, T_CC, and P_CC. The groups composed by the oligomers P_AL and P_AR had similar fluorescence compared to that of the control. The fluorescence decreased significantly for all materials after 6 months of water storage (Figure 1).

Translucency parameter

The translucency parameter in most thio-urethane groups was significantly lower than that of the control in the initial evaluation (up to 36.5%, with T_AR), except for P_AR. Groups P_AR and T_AL were the only ones showing similar translucency in relation to that calculated for control after 6 months. Reduction reached up to 30.5% with P_CC. A significant increase in translucency after 6 months could be observed in groups P_AR, T_AL, T_AR, and T_CC (Figure 2A).

Contrast ratio

In the initial evaluation, a significantly higher contrast ratio was observed for thio-urethane groups in comparison to control (except for P_AR). Resin cements formulated with T_AR, T_CC, and P_CC had significant higher contrast ratio in comparison to the other thio-urethane groups. After 6 months, thio-urethane groups also showed significant higher contrast ratio than that of the control (except for P_AR). The P_CC group showed contrast ratio values that were similar to that obtained for T_CC. A significant decrease in the contrast ratio was observed for groups P_AR, T_AL, T_AR, and T_CC after 6-month water storage (Figure 2B).

Whiteness index for Dentistry (WI_D)

In the initial evaluation, the use of thio-urethane oligomers in the resin cements showed similar WI_D only for the oligomer versions P_AR and T_AL in comparison to control. After 6 months, only the P_AR, T_AL, and T_AR version of thio-urethanes were similar in WI_D in comparison to control. Reductions in TU groups in relation to control were up to 6.1% in the initial evaluation (with P_AL, P_CC, and T_CC) and after six months (with P_CC). A significant increase in the WI_D values after 6 months was observed in groups P_AL, P_AR, T_AL, T_AR, and T_CC (Figure 3A).

Lightness

Similar lightness values were observed for the control group and resin cements composed by P_AR and T_AL in the initial evaluation and after 6 months. The other thio-urethane groups showed significantly lower lightness values than that measured for the control. An increase in lightness was observed after 6 months for the groups control, P_AL, P_AR, T_AR, and T_CC (Figure 3B).

Color difference in transmittance

There were no statistical differences among the color variation values (CIEDE2000, ΔE_{00}) obtained for all evaluated groups. The mean values varied from 1.11 to 1.69, which are below the acceptability threshold value of 1.77 (Figure 4A).[19]

Chroma

Significant higher chroma values were observed for resin cements composed by thio-urethanes in comparison to the control group either in the initial evaluation or after 6 months. The highest values of chroma were presented by the P_CC version of oligomer. An increase in chroma after 6 months was observed for the resin cements composed by P_CC and P_AL (Figure 4B).

Discussion

The first null hypothesis of this study was rejected as the use of some thio-urethanes significantly affected the optical properties (contrast ratio, translucency parameter, and fluorescence) of the RCs. The second hypothesis was partially rejected as some of the color parameters (chroma and lightness) were affected. These optical properties and color parameters are clinically relevant because they represent the complex phenomena of light transmission and reflection which define the tooth color appearance (such as in the case of fluorescence), and are also important to match color characteristics of the restorations to that of natural teeth by means of optical properties such as contrast ratio and translucency parameter. Therefore, the use of thio-urethanes can be harnessed to tailor esthetic characteristics of the resin cements. This can be useful especially in situations where the cement is seen through the prosthetic materials, such as is the case for laminate veneers.

The literature suggests that the translucency of a material is dependent on light absorption and scattering.[20,21]In general, light absorption is produced by the organic matrix while scattering is, among other factors, due to porosity and differences in refractive index mismatch of organic matrix and filler particles.[20] Previous studies suggested that the addition of oligomers to RCs would reduce the mismatch in refractive index between organic matrix and filler particles.[6,7] In the specific case of dental composites, the addition of high refractive index thio-urethane oligomers has been demonstrated to significantly reduce this mismatch.[22] Studies also suggest that differences in the refractive index of the monomers that compose the organic matrix might influence the optical properties, such as the material's translucency.[23,24] This effect is not expected for monomers that form a single phase solution, but may be a consideration when high molecular weight oligomers are used – in those cases, even if to the naked eye it may appear that the materials are completely translucent (or forming a single phase), some light scattering by the thio-urethane oligomers may result at the lower wavelengths. If the wavelength coincides with the radius of gyration of the thio-urethane, according to the Rayleigh scattering theory, some light diffraction can be expected.[25] Therefore, the higher contrast ratio (which translates into greater opacity) and lower translucency parameter (TP_{00}) in RCs containing thio-urethanes compared to the control are possibly due to differences in refractive index of the components of the organic matrix.

The use of thio-urethanes did not increase in the WI_D in the present study. The recent literature has pointed out as relevant a proper measurement of whiteness in research and manufacturing of dental materials.[14] A white material, explained in spectral terms, is one with the constant and high reflectance across the visible wavelength (near to 100% or reflectance value of 1).[14,15] Perceptually, whiteness has lightness and color as components. For luminance, the brighter something is, the whiter it appears. According to color, generally, shades that deviate too far from the white point are deemed to be less white than those of the same luminance. However, humans have a marked preference for 'bluish' white. Therefore, when increasing the bluish color of a sample it will probably be described as 'white'. Whiteness indices capture both of these components.[14]

Fluorescence is the absorption of light and the spontaneous emission of light in a longer wavelength. In general, fluorescent additives need to be incorporated to dental materials in order to increase the amount of light returned back to the observer.[26] Therefore, the development of materials with an increased fluorescence is desirable in Dentistry. The present study showed that it is possible to increase the fluorescence of RCs by using specific thio-urethane oligomers such as T_AR, T_AL, T_CC, and P_CC. This may be explained by the presence of aromatic groups and thio-carbamate bonds on the backbone of the oligomer – these functionalities may have interacted with the wavelengths of light reaching the composite, leading to the interferences that generate fluorescent phenomena. This has been demonstrated for urethanes in RAMAN spectroscopy studies, and those findings can be extrapolated to the interactions observed here.[27] The increase in the refractive index of the organic matrix provided by the addition of oligomers may also explain the increase in fluorescence.[6,7] The reduction in fluorescence observed in all RCs after ageing might be explained by the leaching of components such as unreacted monomers and filler particles to the aqueous medium, which was also observed in previous studies that evaluated the fluorescence of resin-based materials after ageing.[28]

The color difference in transmittance was used to measure the color changes suffered by the RCs over the 6 month water storage. The new RCs formulated with oligomers presented ΔE_{00} values from 1.11 to 1.69 and went through similar color changes as the control group (ΔE_{00} = 1.62). Moreover, all ΔE_{00} values observed in the study were lower than the acceptability threshold of 1.77 established in literature.[19] That means color alteration suffered by materials could be clinically detected, but considered as non-relevant. The results showed that besides the improvement of some of the optical properties presented above, the RCs composed by oligomers cannot be considered more susceptible to color changes than RCs formulated only with traditional monomers such as BisGMA/UDMA/TEGDMA.

The parameters of lightness and chroma were also affected by the addition of thio-urethanes. Although these parameters were more relevant in the context of the present study to calculate the TP_{00} value, their individual values also present clinical relevance as they can influence the shades of the composite produced with the thio-urethane oligomers. Lightness is defined as the degree of black and white of a material, with lighter materials having a predominance of the white component. Chroma represents the saturation of a color. Reduction in lightness was observed in most RCs formulated with oligomers in comparison to the control group either in the initial evaluation or after 6 months of water storage. All RCs composed of oligomers had an increase in chroma in comparison to the control. A few possible explanations can be hypothesized. First, in experimental composites such as the ones used in the present study, the filler component is mainly responsible for the color of the material, especially in parameters such as chroma and lightness.[29] With the increase in light transmission given by the better match in refractive indices between organic matrix and inorganic fillers achieved with the oligomers, as well as the increased conversion,[22] it is possible that the fillers were more “visible”, explaining the increase in chroma. This increase in chroma might be one possible disadvantage in the case of the ultra-thin porcelain veneers. The reduction in lightness is more difficult to explain, as the increase in light transmission should have also made the component with more “white” to be exposed, and therefore, increased the lightness. One hypothesis is the fact that carbamates and aromatics present absorption in certain wavelengths, and that might have reduced the white component of the system. UV-Vis experiments with the organic component only are planned for future studies to help elucidate this hypothesis.

Considering resin cements, the influence of their color and optical properties on the final appearance will highly depend on the characteristics of the indirect restoration. For example, materials used for indirect restorations present a variety of translucency, and the influence of the resin cement will be lower as less translucent the restorative material of choice. In the same aspect, different thickness of restorations are adopted depending on the amount of dental tissue lost or the need to mask discolored substrates. In this way, the resin cement will have a lower effect on the final appearance with thicker restorations. Another point worth to mentioning is that the resin cement film-thickness suggested by ISO 4049[30] is 50 μm and, for methodological reasons, a much thicker specimen was adopted in this study, which might have influence on the extrapolation of the results to a clinical scenario.

Conclusion

Within the limitations of this study, results showed that resin cements containing thio-urethane oligomers have higher contrast ratio and lower translucency. Depending on the type of oligomer used, higher fluorescence was depicted.

Resin cements composed by the oligomers showed higher chroma. However, the color alteration (ΔE_{00}) observed for thio-urethane-based resin cements after 6 months of water storage was similar than that observed for the control group composed by pure BisGMA/ UDMA/TEGDMA matrix. None of the color difference values surpassed the acceptability threshold suggested by the literature.

Acknowledgement

The authors thank NIH-NIDCR (1R15-DE023211–01A1 and 1U01-DE02756–01) and FAPESP 2017–11913–8 for financial support. The donation of methacrylate monomers by Esstech is also greatly appreciated.

REFERENCES

1. Manso AP, Silva NRFA, Bonfante EA, TA Pegoraro, RA Dias, Carvalho RM. Cements and Adhesives for all-ceramic restorations. Dent Clin North Am 2011; 55:311–32. [PubMed: 21473996]

2. Bacchi A, Dobson A, Ferracane JL, Consani RL, Pfeifer CS. Thio-urethanes improve properties of dual-cured composite cements. J Dent Res 2014; 93:1320–5. [PubMed: 25248610]
3. Bacchi A, Consani RL, Martim GC, Pfeifer CS. Thio-urethane oligomers improve properties of light-cured resin composites. Dent Mater 2015; 31:565–74. [PubMed: 25740124]
4. Bacchi A, Pfeifer CS. Rheological and mechanical properties and interfacial stress development of composite cements formulated with thio-urethane oligomers. Dent Mater 2016; 32:978–86. [PubMed: 27257101]
5. Pfeifer CS, Wilson ND, Shelton ZR, Stansbury JW. Delayed gelation through chain-transfer reactions: mechanism for stress reduction in methacrylate. Polymer 2011; 52:3295–303. [PubMed: 21799544]
6. Li Q, Wicks DA, Hoyle CE. Thiouretane-Based Thiol-Ene High T_g Networks: Preparation, Thermal, Mechanical, and Physical Properties. J Polymer Sci Part A: Polym Chem 2007; 45: 5103–11.
7. Shin J, Matsushima H, Comer CM, Bowman CN, Hoyle CE. Thio-Isocyanate-Ene Ternary Networks by Sequential and Simultaneous Thiol Click Reactions. Chem Mater 2010; 22:2616–25.
8. Bacchi A, Nelson M, Pfeifer CS. Characterization of methacrylate-based composites cointaining thio-urethane oligomers. Dent Mater 2015; 32:233–9.
9. Bacchi A, Yih J, Platta J, Knight J, Pfeifer CS. Shrinkage / stress reduction and mechanical properties improvement in restorative composites formulated with thio-urethane oligomers. J Mech Behav Biomed Mater 2018; 78:235–40. [PubMed: 29175492]
10. Bacchi A, Spazzin AO, Oliveira GR, Pfeifer C, Cesar PF. Resin cements formulated with thio-urethanes can strengthen porcelain and increase bond strength to ceramics. J Dent 2018; 73:50–56. [PubMed: 29630920]
11. Rafael CF, Guth JF, Kauling AEC, Cesar PF, Volpato CAM, Liebermann A. Impact of background on color, transmittance, and fluorescence of leucite-based ceramics. Dent Mater J 2017; 36:394–401. [PubMed: 28367913]
12. Johnston WM. Review of translucency determinations and applications to dental materials. J Esthet Res Dent 2014; 26:217–23.
13. Vichi A, Carrabba M, Paravina R, Ferrari M. Translucency of ceramic materials for CEREC CAD/CAM system. J Esthet Restor Dent 2014; 26:224–31. [PubMed: 24974858]
14. Joiner A, Hopkinson I, Deng Y, Westland S. A review of tooth colour and whiteness. J Dent 2008;36s:s2–7. [PubMed: 18646363]
15. Pérez MM, Ghinea R, Rivas MJ, Yebra A, Ionescu AM, Paravina RD, Herrera LJ. Development of a customized whiteness index for Dentistry based on CIELAB color space. Dent Mater 2016; 32:461–7. [PubMed: 26778404]
16. Salas M, Lucena C, Herrera LJ, Yebra A, Della Bona A, Pérez MM. Translucency thresholds for dental materials. Dent Mater 2018 (in press) doi: 10.1016/j.dental.2018.05.001.
17. Luo MR, Cui G, Rigg B. The development of the CIE 2000 color difference formula: CIEDE2000. Col Res Appl 2001;26:340–50.
18. Commission Internationale de l´Eclairage. CIE Technical Report: Colorimetry CIE Pub No. 15.3. Vienna: CIE Central Bureau; 2004.
19. Paravina RD, Ghinea R, Herrera LJ, Bona AD, Igiel C, Linninger M, Sakai M, Takahashi H, Tashkandi E, Perez Mdel M. Color difference thresholds in dentistry. J Esthet Restor Dent 2015;27:S1–9. [PubMed: 25886208]
20. Shortall AC, Palin WM, Burtscher P. Refractive index mismatch and monomer reactivity influence composite curing depth. J Dent Res 2008; 87:84–8. [PubMed: 18096900]
21. Yu B, Ahn JS, Lee YK. Influence of TiO2 nanoparticles on the optical properties of resin composites. Dent Mater 2009; 25:1142–7. [PubMed: 19410287]
22. Faria-e-Silva AL, Pfeifer CS. Impacto f thio-urethane additive and filler type on light-transmission and depth of polymerization of dental composites. Dent Mater 2017; 33:1274–85. [PubMed: 28807329]
23. Miletic V, Jakovljevic N, Manojlovic D, Marjanovic J, Rosic AA, Dramicanin MD. Refractive indices of unfilled resin mixtures and cured composites related to color and translucency of

conventional and low-shrinkage composites. J Biomed Mater Res B Appl Biomater 2017; 105:7–13. [PubMed: 26372168]

24. Ota M, Ando S, Endo H, Ogura Y, Miyazaki M, Hosoya Y. Influence of refractive index on optical parameters of experimental resin composites. Acta Odontol Scand 2012; 70:362–7. [PubMed: 21780980]
25. Santos GB, Medeiros IS, Fellows CE, Muench A, Braga RR. Composite depth of cure obtained with QTH and LED units assessed by microhardness and micro-Raman spectroscopy. Oper Dent 2007; 32:79–83. [PubMed: 17288333]
26. Sikri VK. Color: implications in dentistry. J Conserv Dent 2010; 13:249–55. [PubMed: 21217954]
27. Pfeifer CS, Silva LR, Kawano Y, Braga RR. Bis-GMA co-polymerizations: influence on conversion, flexural properties, fracture toughness and susceptibility to etanol degradation of experimental composites. Dent Mater 2009; 25:1136–41. [PubMed: 19395016]
28. Antonov M, Lenhardt L, Manojlovic D, Milicevic B, Zekovic I, Dramicanin MD. Changes of color and fluorescence of resin composites immersed in beer. J Esthet Restor Dent 2016; 28:330–38. [PubMed: 27439759]
29. Suh YR, Ahn JS, Ju SW, Kim KM. Influences of filler content and size on the color adjustment potential of nonlayered resin composites. Dent Mater J 2017; 31:35–40.
30. Standard I ISO 4049 polymer based filling, restorative and luting materials. International Organization for Standardization; 2000 p. 1–27.

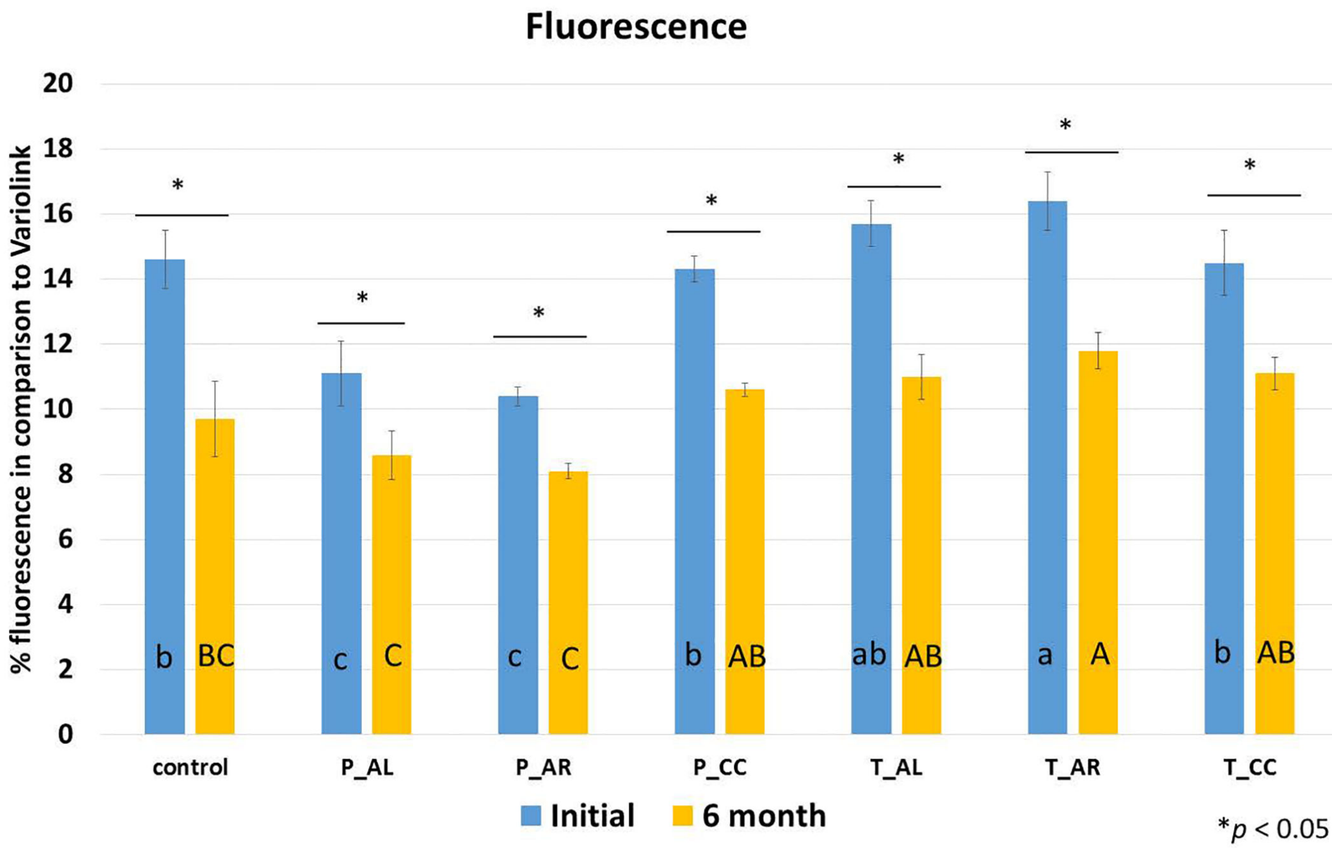

Figure 1.

Means and standard deviation values of fluorescence for the groups tested after 72h storage ("initial") in dark containers and 6 month-storage in distilled water. Different lowercase letters indicate statistical difference among the groups in the initial analysis whilst different capital letters show statistical difference among the groups after 6 months ($p<0.05$). The asterisks (*) denote statistical significance between the groups of the same material tested in different storage periods.

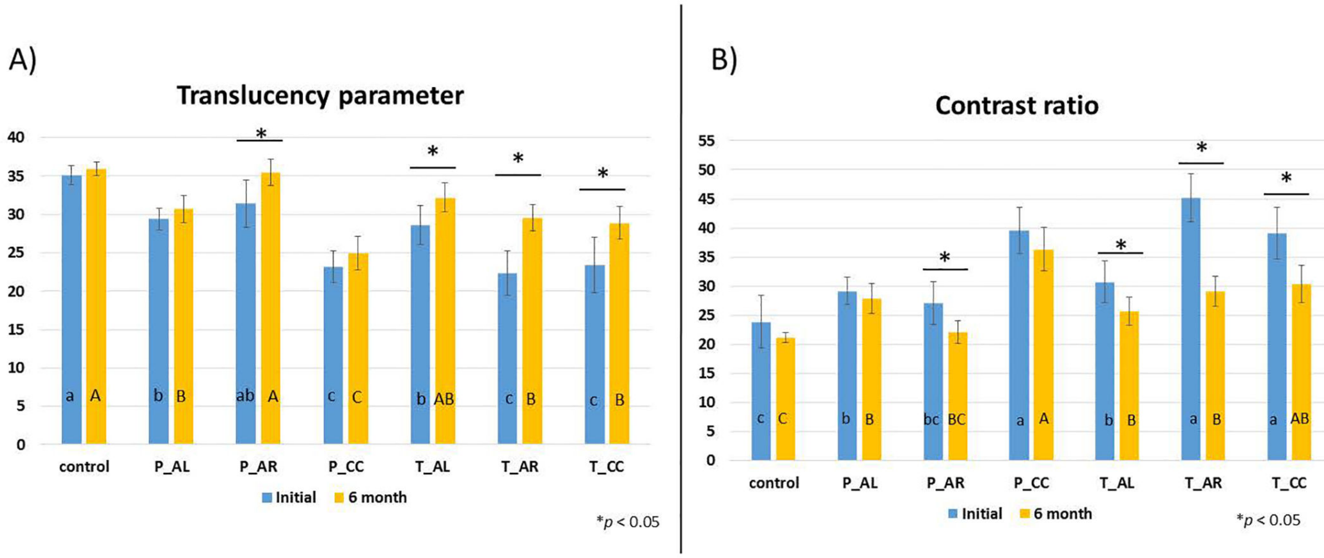

Figure 2.

Means and standard deviation values of (A) translucency parameter and (B) contrast ratio for the groups tested after 72h storage (“initial”) in dark containers and 6 month-storage in distilled water. Different lowercase letters indicate statistical difference among the groups in the initial analysis whilst different capital letters show statistical difference among the groups after 6 months ($p<0.05$). The asterisks (*) denote statistical significance between the groups of the same material tested in different storage periods.

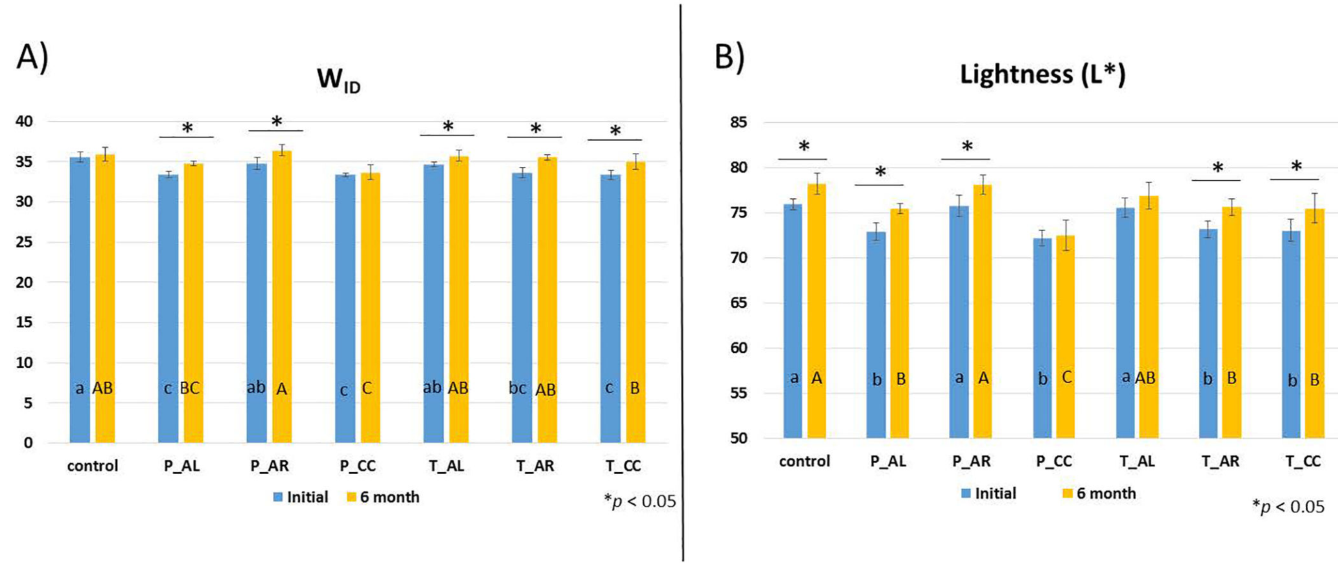

Figure 3.

Means and standard deviation values of (A) whiteness index for dentistry (WI_D) and (B) lightness for the groups tested after 72h storage (“initial”) in dark containers and 6 month-storage in distilled water. Different lowercase letters indicate statistical difference among the groups in the initial analysis whilst different capital letters show statistical difference among the groups after 6 months ($p<0.05$). The asterisks (*) denote statistical significance between the groups of the same material tested in different storage periods.

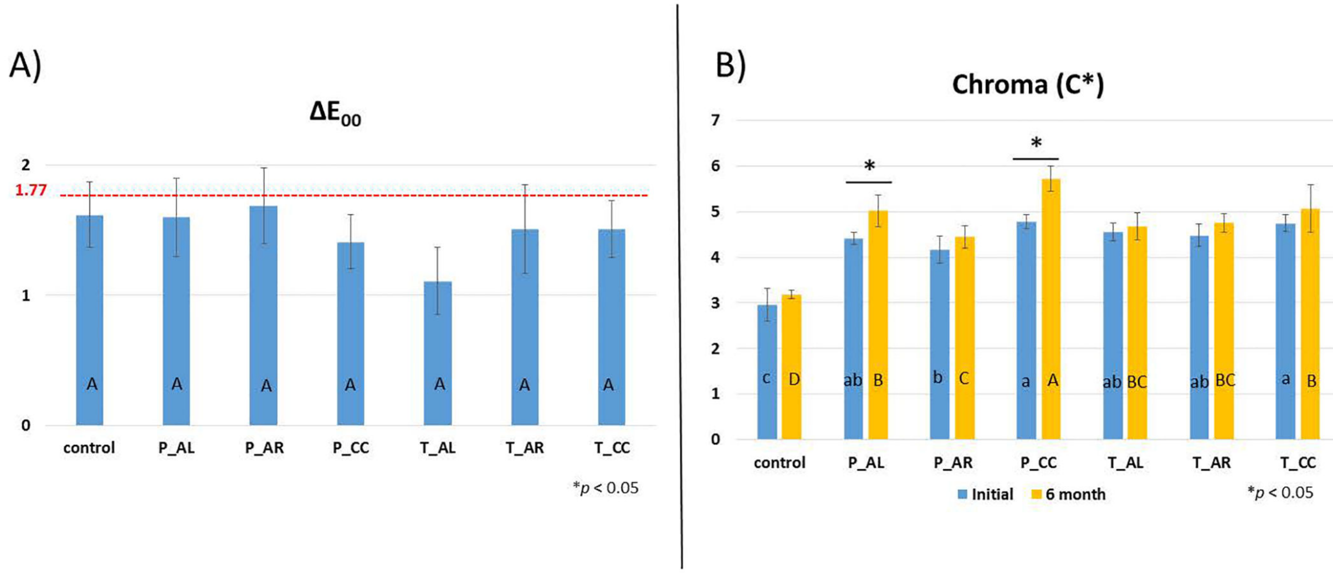

Figure 4.

Means and standard deviation values of (A) color difference in transmittance (ΔE_{00}) of each resin cement before and after 6 months of water storage and (B) chroma for the groups tested after 72h storage ("initial") in dark containers and 6 month-storage in distilled water. Different lowercase letters indicate statistical difference among the groups in the initial analysis whilst different capital letters show statistical difference among the groups after 6 months (p<0.05). The asterisks (*) denote statistical significance between the groups of the same material tested in different storage periods.

Table 1.

Combination of isocyanates with thiols for the composition of the six thio-urethane oligomers used in the study.

Thiol (abbreviation)	Isocyanate (abbreviation)	Thio-urethane formed
Pentaerythritol tetra-3-mercaptopropionate (PETMP)	1,6-Hexanediol-diissocyante (aliphatic, AL)	P_AL
Pentaerythritol tetra-3-mercaptopropionate (PETMP)	1,3-bis(1-isocyanato-1-methylethyl)benzene (aromatic, AR)	P_AR
Pentaerythritol tetra-3-mercaptopropionate (PETMP)	Dicyclohexylmethane 4,4'-Diisocyanate (cyclic, CC)	P_CC
Trimethylol-tris-3-mercaptopropionate (TMP)	1,6-Hexanediol-diissocyante (aliphatic, AL)	T_AL
Trimethylol-tris-3-mercaptopropionate (TMP)	1,3-bis(1-isocyanato-1-methylethyl)benzene (aromatic, AR)	T_AR
Trimethylol-tris-3-mercaptopropionate (TMP)	Dicyclohexylmethane 4,4'-Diisocyanate (cyclic, CC)	T_CC